

Corrosion Inhibition Effect of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one Inhibitor for Mild Steel in 1 M HCl Solution

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ABSTRACT

The environmental friendly 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one (A1) inhibitor is synthesized and their corrosion inhibition for Mild Steel in a 1 M HCl solution was studied using weight loss methods, electrochemical measurements, and the surface morphology of mild steel with and without inhibitor were studied using scanning electron microscopy (SEM) analysis. The inhibition efficiency of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1, 3, 4-oxadiazol-2-yl) propan-1-one improved with increases in inhibitor concentration but decreased with increases in temperature. Results from potentiodynamic polarization and EIS showed that the corrosion inhibition efficiency of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1, 3, 4-oxadiazol-2-yl)propan-1-one was excellent. Morphology observation revealed that the Mild Steel was greatly protected by these 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one inhibitor.

Keywords: Mild Steel; potentiodynamic polarization; EIS, corrosion inhibition

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INTRODUCTION

Corrosion of aluminum and its alloys has attracted much attention from many researchers due to their high mechanical intensity, low cost, low density, and good machinability, and they have been widely used in industrial applications, especially in constructions, electronics, packing, storage, and transportation equipment and machinery [1-6]. Corrosion is an electrochemical process and is often activated by industrial processes such as acid descaling, acid pickling, acid

cleaning, and oil well acidizing [7]. Efforts have been made to protect the integrity of the aluminum surface in an aggressive acid medium or other corrosive environment. In recent decades, the addition of inhibitors has been considered to be the most common approach to hinder the corrosion of aluminum [7-10].

Many organic compounds have been widely reported as corrosion inhibitors of aluminum in acid solution, such as aliphatic, aromatic amines, and nitrogen heterocyclic

molecules [11–15]. However, some of these compounds are costly and not easily biodegradable. As high reactive, low cost, high solubility, and environmentally friendly compounds, triazinedithiol, and its monosodium salt have been reported to prepare the effective corrosion inhibitive film on metal surfaces by electrochemical deposition [16–19]. The special tautomer of thiol–thione with highly electronegative atoms like S and O, and the N-containing heterocyclic conjugate system, benefit the 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one molecules to adsorb on metallic surface. However, the research on 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one inhibitors for Mild Steel is seldom reported. The purpose of present work is to investigate and compare the corrosion inhibition action of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one and their protective performance for Mild Steel (MILD STEEL) in 1 M HCl was studied utilizing a variety of electrochemical tests, weight loss methods, scanning electron microscopy (SEM) techniques.

MATERIALS AND METHODS

Materials and Sample Preparation

The Mild Steel sheet having chemical composition is as follows:

Table 1: Chemical Composition of Mild Steel

Chemical	Composition
Carbon	0.16-0.18%
Silicon	0.40% max
Manganese	0.70-0.90%
Sulphur	0.040% Max
Phosphorus	0.040% Max

MS was mechanically press-cut into specimens of dimension 30 mm × 50 mm × 0.3 mm. All test plates of MILD STEEL were ultrasonically degreased in the acetone for 15 min, and

treated by the immersion in alkaline solution (15 g Na₂CO₃ + 15 g Na₂PO₄ per liter) at 60 °C for the debinding process [20]. After that, the Mild Steel specimens were washed thoroughly with distilled water and dried with nitrogen. The specimens with an exposed area of 1 cm² were used for potentiodynamic polarization and electrochemical impedance spectroscopy. AR (analytical reagent) grade hydrochloric acid and double distilled water were used to prepare the corrosive media. In this paper, Synthesis of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one Aryl hydrazide (1 M) was dissolved in phosphorous oxychloride (5 mL). The reaction mixture, after refluxing for 6-7 hours, was cooled to room temperature and poured onto crushed ice. On neutralization of the contents with sodium bicarbonate solution (20%), a solid mass separated out. This was filtered and washed with water. It was crystallized by using methanol 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one and Yield 89.90%, yellow powder, mp (°C): 240–242.

Electrochemical Measurements

The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were carried out using CHI 608E electrochemical work station (CHI Instruments; USA) in a three-electrode cell system with a saturated calomel electrode (SCE) as reference electrode and a rectangular piece of graphite as counter electrode. The working electrode was MILD STEEL. Prior to any electrochemical measurements, the immersion in the solution for 1 h was necessary for the open circuit potential to reach a steady state. EIS was carried out at steady open circuit potential disturbed with amplitude of 10 mV alternative current sine wave in the frequency range of 100 MHz to 10 kHz. The polarization curves were obtained by changing potential from –250 mV to +250 mV versus OCP with a scan rate of 0.5 mV/s.



Figure 1: Experimental set up for potentiodynamic and EIS studies

Scanning Electron Microscopy (SEM)

The surfaces morphologies of the Mild Steel immersed in a 1 M HCl solution for 2 h with and without the 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one inhibitors were observed via SEM (JSM-6360LV, JEOL, Tokyo, Japan) at an accelerating voltage of 20 kV, respectively.

RESULTS

Potentiodynamic Polarization

Potentiodynamic polarization profiles for MILD STEEL with different concentrations of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one are presented in Figure 2. The corrosion kinetics parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and cathodic and anodic Tafel slopes (β_a , β_c) were given in Table 2, where the inhibition efficiency η_p (%) was calculated.

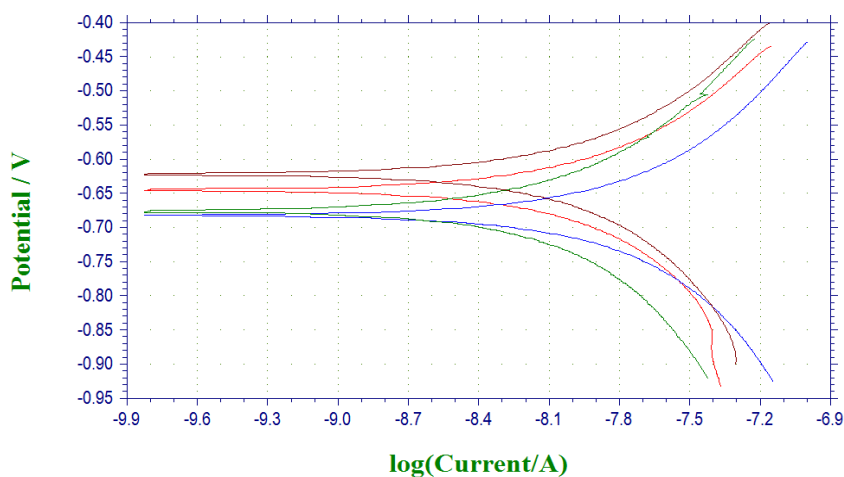


Figure 2: Tafel plots for Mild Steel in 1 M HCl containing different concentrations of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one

Compared with the blank solution, the cathodic currents were significantly decreased with the presence of inhibitors and the addition of these compounds made E_{corr} shifted towards negative potentials (Figure 2), which suggested that 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one greatly reduced the hydrogen evolution

reaction, but their inhibition effects on the anodic dissolution were unobvious. Besides, the addition of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one shift the cathodic and anodic curves to lower values, while the concentration of inhibitors was increased.

Table 2: Tafel polarization parameters of the corrosion for Mild Steel in 1 M HCl containing different concentrations of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one

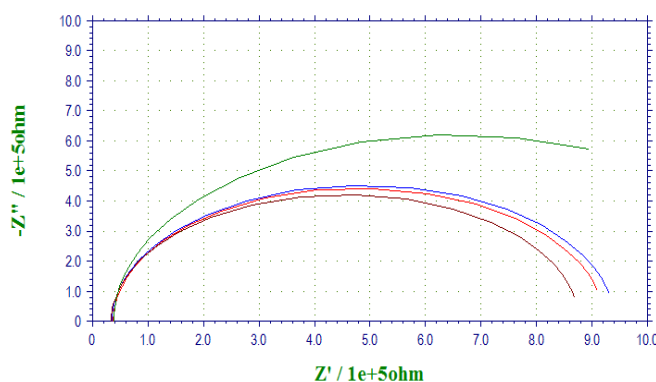
Inhibitor	C (ppm)	E_{corr} (mV/SCE)	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	β_a (mV·dec ⁻¹)	β_c (mV·dec ⁻¹)	η_p (%)
A1	Blank	-735.90	2852.40	118.30	90.50	Blank
	50	-742.10	835.30	128.30	88.70	70.72
	100	-739.00	316.50	136.50	96.40	88.90
	150	-740.40	251.90	140.10	90.80	90.17

From Table 2, it is clearly seen that, when more inhibitors were added into the corrosive solution, the corrosion current density decreased and the inhibition efficiency increased. When the concentration of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one reached 1 mM, the lowest I_{corr} values of $63.6 \mu\text{A}\cdot\text{cm}^{-2}$ and $33.5 \mu\text{A}\cdot\text{cm}^{-2}$ were obtained, and the inhibition efficiency achieved 97.77% and 98.83%, respectively. Generally, a compound is considered to anodic or cathodic type when the displacement in E_{corr} is greater than 85 mV; otherwise, inhibitor is considered as a mixed type [21]. For 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one, the E_{corr} values shift towards more a negative direction compared with the blank solution, but the change is not significant when the maximum displacement of E_{corr} values is 10.9 mV, which indicated that 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one belonged to mixed-type inhibitors, mainly inhibiting the cathodic processes.

Electrochemical Impedance Spectroscopy (EIS)

Nyquist plots for Mild Steel in the absence and

presence of various concentrations of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one are given in Figure 3. The impedance spectra are consisted of capacitive loops at higher frequency and inductive loops at lower frequency. The presence of depressed semicircle in Nyquist plot across the studied frequency range indicates that a charge transfer process mainly controls the corrosion of aluminum. In other literature, similar plots have been reported for the corrosion of aluminum alloys in HCl solutions [20]. The inductive loop is generally attributed to the relaxation process in the oxide film covered on metal surface [22]. The reasons behind the deviations from perfect semicircles are usually involved with the frequency dispersion of interfacial impedance, which can be attributed to various kinds of physical phenomena such as active sites, surface roughness, and non-homogeneity of the solids [23]. The diameter of the capacitive loop is enlarging gradually with increasing concentrations of inhibitor, indicating that the charge transfer resistance is increased and the adsorbed inhibitor forms a more compact monolayer on metal surface with an increasing amount of inhibitor.

**Figure 3: Nyquist diagrams for Mild Steel in 1 M HCl containing different concentrations of 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one**

Surface Morphology

SEM technique was employed to further prove the corrosion resistance ability of DAN and DBN, and the surface observation images of Mild Steel after a 2 h exposure in a HCl solution without and with inhibitors are shown in Figure 4. Before immersion, the bare aluminum plate looks very smooth (Figure 4a). In contrast, in the absence of inhibitor, the MILD STEEL presented a very rough surface covered with a huge amount of deep cracks and large holes, which suggests strong damage and a severe dissolution of Mild Steel

in contact with aggressive solution (Figure 4b). Nevertheless, in Figure 4c,d, the dissolution rate of Mild Steel was substantially inhibited by DAN and DBN, exhibiting a comparative smooth surface with a few small pits. Therefore, it is concluded that the regular distribution of the DAN or DBN molecules adsorbed on MILD STEEL surface generates consistent protective layers, which effectively prevent HCl molecules from penetrating into the aluminum surface.

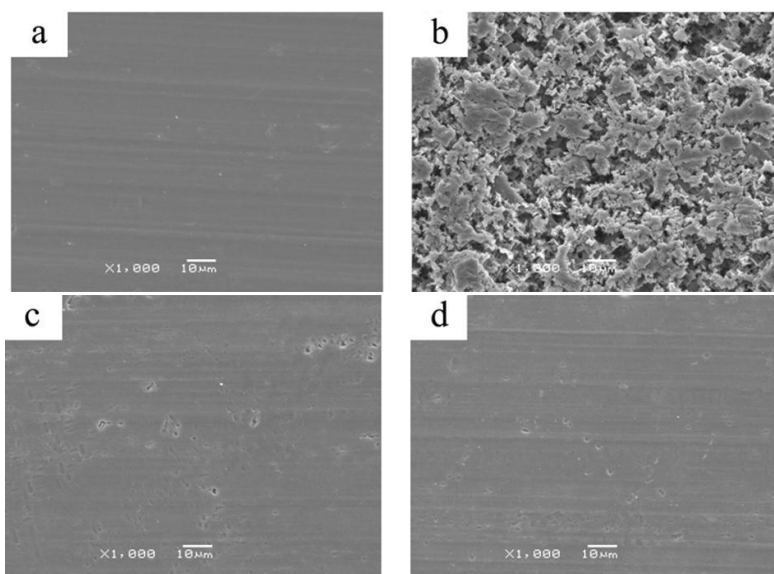


Figure 4: SEM images of MILD STEEL surface before and after immersing in 1 M HCl without and with 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one inhibitor. (a) Blank before immersion; (b) blank after immersion; (c) with 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one(50ppm) (d) with 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one(150ppm)

Mechanism of inhibition

Corrosion inhibition of mild steel in 1M hydrochloric acid solution by 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one inhibitor can be explained on the basis of molecular adsorption. These compounds inhibit corrosion by controlling both anodic as well as cathodic reactions. In 1M hydrochloric acid solution this inhibitor exists as protonated species. In the inhibitor the nitrogen atoms present in the molecules can be easily protonated in acidic solution and convert into quaternary compounds. These protonated species adsorbed on the cathodic

sites of the mild steel and decrease the evolution of hydrogen.

CONCLUSIONS

1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one compound as corrosion inhibitors for Mild Steel in a 1 M HCl solution were investigated. For 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one, their inhibition efficiency increased with increases in inhibitor concentration and they belonged to mixed-type inhibitors predominantly retarding the

cathodic reaction. The inhibiting efficiencies determined by potentiodynamic polarization testing, and EIS measurements are all in good agreement. The surface morphologies images were good proof for the reduction of dissolution of Mild Steel ascribed to the formation of protective 1-(4-Methoxy-phenyl)-3-(5-phenyl-1,3,4-oxadiazol-2-yl)propan-1-one film on the metal surface.

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